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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C04B 28/18, 28/20, 38/00, 38/08, 40/00</b>		<b>A1</b>	(11) International Publication Number: <b>WO 00/21901</b>
			(43) International Publication Date: 20 April 2000 (20.04.00)
(21) International Application Number: <b>PCT/AU99/00875</b>		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 13 October 1999 (13.10.99)			
(30) Priority Data: PP 6501 14 October 1998 (14.10.98) AU			
(71) Applicant (for all designated States except US): JAMES HARDIE RESEARCH PTY LIMITED [AU/AU]; 2nd floor, 1 Grand Avenue, Camellia, NSW 2142 (AU).			
(72) Inventors; and (75) Inventors/Applicants (for US only): BLACK, Andrew [AU/AU]; 8A Adolphus Street, Naremburn, NSW 2065 (AU). CHEN, Hong [AU/AU]; 10 Barnsbury Grove, Bexley North, NSW 2207 (AU). GLEESON, James [AU/US]; Apt. 3406, 10655 Lemon Avenue, Alta Loma, CA 91737 (US). PARKS, Sean [US/US]; 14644 Nova Scotia Drive, Fontana, CA 92337 (US). KIRBY, Nigel [AU/AU]; 4 Blytheswood Avenue, Warrawee, NSW 2074 (AU). MONEY, Erik [AU/AU]; 7 Harold Avenue, Pennant Hills, NSW 2120 (AU).		Published With international search report.	
(74) Agent: BALDWIN SHELSTON WATERS; 60 Margaret Street, Sydney, NSW 2000 (AU).			

(54) Title: CEMENT FORMULATION

## (57) Abstract

A formulation and method of producing a shaped cementitious article having either a reduced respirable size silica particle content or a low propensity to release air borne respirable silica or both. The formulation comprises cementitious material, a siliceous material and a low bulk density material. The density of the product is preferably 1.2 g/cm<sup>3</sup> or less and the low bulk density is preferably substantially calcium silicate hydrate. The applicant has found that with such a density and/or low bulk density material in the article, the product provides a substantially reduced amount of respirable size silica when cut.

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**TITLE: CEMENT FORMULATION****TECHNICAL FIELD**

The present invention relates to a cement formulation and a method of reducing respirable size silica particles in cementitious shaped articles and the propensity of such articles to liberate airborne respirable silica. The invention relates to all cementitious articles.

**BACKGROUND ART**

The inhalation of dust as a primary cause of pulmonary disease has been a problem in the mining industry since antiquity. The problems were first termed pneumonokoniosis, but the generic term has since been shortened to pneumoconiosis. The word implied that the lung had been seriously damaged by dust, but the meaning has been broadened to include all pulmonary manifestation of dust inhalation. The result of pneumoconiosis is to harden the linings of the lung by creating fibrous growths that make the lung effectively inoperative. Cures are impossible, so prevention is the goal of modern industry.

One of the most important forms of pneumoconiosis is silicosis. The cause of silicosis is primarily inhaled particles of crystalline silicon dioxide or silica ( $\text{SiO}_2$ ), most commonly quartz which is a ubiquitous mineral in nature. Quartz is considered to be chemically inert, reactive only in hydrofluoric and phosphoric acids and strongly basic solutions, but it does react in the lung linings to initiate fibrous tissue growth for unknown reasons. Whether the quartz acts as an irritant, a nucleation site, or is involved in the chemical reactions is not clear. In addition to the supply of personal protective equipment, one technique for prevention of silicosis is to clean up the atmosphere that workers might inhale. Early prevention procedures in "hard rock" mining were to shift from drilling dry to drilling with water flushing the cuttings away from the working face.

Modern practices in mines and industrial plants include directing the affected atmosphere away from the working and into collector systems that remove the respirable particle component before the atmosphere is recirculated. Because of the perceived health hazard of certain crystalline forms of silica in the industrial

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environment, many governments around the world require monitoring the presence of silica forms in the workplace atmospheres and marketed products. The atmosphere and personnel are regularly monitored by sampling devices that can accumulate the particulate matter in a quantitative fashion for subsequent laboratory analysis.

- 5 However, the samples present the analytical laboratory with several challenges, namely the detection of the silica minerals in the sample, the quantification of the amount of crystalline silica in the sample.

- Respirable silica not only arises from production processes but may also arise from use of certain articles. Conventional autoclaved fibre reinforced cement articles  
10 for instance are formulated from a mixture of reinforcement fibre, cementitious material such as ordinary Portland cement, fine quartz, water and other minor additives such as pigments and process aids. The fibre component is added to make the article strong and ductile and is typically refined Kraft cellulose fibre. The fine quartz is typically prepared from normal crystalline silica in the form of sand by wet  
15 grinding.

The typical particle size distribution of ground silica sand, which is normally just called "silica", when taken to the economically practical limit of wet grinding is:

PARTICLE SIZE RANGE	TYPICAL PROPORTION OF GROUND SILICA IN SIZE RANGE
< 1 microns	3%
< 2 microns	10%
< 10 microns	33%
< 20 microns	48%
< 100 microns	95%

- 20 The particle size distribution of the silica is similar to that of ordinary Portland cement, approximately half by mass of the particles in both materials are coarse and

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greater than 20 microns in size and approximately half of the particles are fine and less than 20 microns in size.

High pressure steam autoclaving of such a mixture causes a calcium silicate hydrate (CSH) matrix to be formed, the cement providing the source of calcium (CaO), the fine quartz providing the main source of slightly soluble silica (SiO<sub>2</sub>) and the water providing the hydrate (H<sub>2</sub>O). The CSH matrix is the binder which sets around the fibre and unreacted silica to form fibre cement articles such as building boards. Research has indicated that in such a matrix, the surface of the silica particles is reacted to a depth of approximately 2 microns when the formulation is subjected to the conventional 8 hour high pressure 170°C steam autoclave cycle. The depth of the corresponding CSH skin formed around the silica particles will exceed 2 microns.

Airborne respirable dust is defined by either the ACGIH-ISO-CEN curve (American standard) and/or the BMRC curve (UK/European standard). The generally accepted OSHA occupational exposure standard in the US for airborne respirable quartz over an 8 hour work day is 0.1 mg/m<sup>3</sup> of air (TLV). Conventional fibre reinforced cementitious building boards may contain up to 18% of respirable size silica particles after autoclaving. US regulations require that any product containing more than 0.1 wt % of quartz, cristobalite or tridymite (forms of silica) must be labelled as a potential hazard. Respirable silica may be liberated from conventional building boards for example when they are cut in a dry state using power tools like sanders and circular saws. Such cutting may also increase the liberation quantity of airborne respirable silica from the cementitious article. To explain, the saw blade may in some circumstances grind the larger silica particles to a size that falls within the airborne respirable range.

Previous attempts to reduce the respirable silica levels in cement articles have involved reacting stoichiometric quantities of cement (or other cementitious material) with extremely fine ground, or colloidal, or amorphous silica to form a matrix to bind the reinforcing fibres. Articles manufactured from such formulations can be made to have low respirable quartz contents, but they also have excessive hygroscopic shrinkage and carbonation shrinkage. Such articles also have inadequate strength properties for a given material density compared to those formed from conventional

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formulations. In service such articles are very brittle and tend to crack and split easily because the drying shrinkage and the carbonation shrinkage generated stresses in the material exceed its stress carrying capacity.

The present invention seeks to overcome at least some of the disadvantages of the prior art or provide a commercial alternative thereto.

#### DISCLOSURE OF THE INVENTION

According to a first aspect, the present invention provides a formulation for producing a shaped cementitious article having a reduced respirable size silica particle content, said formulation comprising a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide a density of the resultant cementitious article of lower than  $1.2 \text{ g/cm}^3$ .

According to a second aspect, the present invention provides a formulation for producing a shaped cementitious article having a low propensity to release airborne respirable silica, said formulation comprising a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide a density of the resultant cementitious article of lower than  $1.2 \text{ g/cm}^3$ .

As discussed above, it is generally accepted that respirable silica includes particles smaller than approximately 5 microns. Cementitious articles may already contain unreacted silica which falls within this respirable range. This is termed respirable size silica particles. Additionally, silica particles which are larger than 5 microns may be reduced to the respirable range during cutting or grinding to form airborne respirable silica particles. The applicant believes that the present inventive formulation not only reduces the quantity of respirable size silica particles in the cementitious article but reduces the propensity for airborne respirable silica to be formed or liberated during use, cutting, grinding etc of the cementitious article.

The person skilled in the art will be aware of appropriate low bulk density modifiers for shaped cementitious articles. They include materials such as fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene, fly ash, hollow fly ash, hollow ceramic spheres and chemical or mechanical gas entrainment.

Preferably, however, the low bulk density material is made up of particles being substantially calcium silicate hydrate, typically in the form of a 3-D interlocking

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structure and is resistant to crushing in subsequent processing. In other preferred forms, mixtures of calcium silicate hydrate and any other low bulk density material may be used.

According to a third aspect, the present invention provides a formulation for  
5 producing a shaped cementitious article having a reduced respirable size silica particle content, said formulation comprising a cementitious material, a siliceous material and a low bulk density material being substantially calcium silicate hydrate.

According to a fourth aspect, the present invention provides a formulation for  
10 producing a shaped cementitious article having a low propensity to release airborne respirable silica, said formulation comprising a cementitious material, a siliceous material and a low bulk density material being substantially calcium silicate hydrate.

Preferably, the low bulk density material has a bulk density of between 0.06 and 0.6 g/cm<sup>3</sup>. The low bulk density material may be provided by reacting a siliceous reactant with a calcareous reactant in the presence of water under pressure and  
15 elevated temperature. More preferably, at least 90 wt % of the siliceous reactant has a particle size of less than 100 microns.

The applicant has found that the shaped article produced from the abovementioned formulation produces less respirable quartz when cut or ground as compared with conventional cementitious articles. It is not entirely understood by the  
20 applicant why the reduction in respirable silica occurs. Not wishing to be bound by any particular theory, the applicant has hypothesised several reasons for this phenomenon, namely:

a) the cement formulation is of a low density type. The unreacted silica in the cement formulation, however, is of a relatively high density. When struck with a  
25 saw or grinder, therefore, the unreacted silica particle is either embedded into the low density cement or removed as a whole piece from the article. The unreacted silica particles are not ground by the cutting or grinding means. The cutting action is a true cutting action. The blade slices between the unreacted silica particles and the remaining cement rather than grinding through the silica particles. The removed silica  
30 particles are quite large and do not fall within the "respirable" range.

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b) cementitious articles produced from the preferred formulation provide less surface area when cut for release of the airborne respirable silica. To explain, conventional cementitious articles with higher densities eg  $1.4 \text{ g/cm}^3$  and above, tend to break and provide a jagged rough edge when cut. A cementitious article formed from the formulation defined in any of the first through fourth aspects, however, provides a smooth edge when cut. This in turn reduces the available surface area for liberation of the airborne respirable silica and accordingly less airborne respirable silica is released.

c) the quantity of prereacted calcium silicate hydrate in the formulation reduces the quantity of unreacted silica which may form respirable silica,

d) since a substantial portion of the calcium silicate hydrate is already provided as a prereacted product, there is a reduction in the quantity of siliceous material which undergoes a reaction with the cementitious material to form the CSH matrix. As mentioned above, the CSH reaction may reduce the size of the silica particles rendering them potentially "respirable". Less reacted silica particles mean less potential "respirable" silica.

In its preferred form, the low bulk density material, which is substantially CSH, also has a substantially spherical shape. The outer skin is calcium silicate hydrate. The inner portion may include unreacted silica if, as is preferred, the reaction to form CSH is terminated prior to complete conversion. The CSH skin is, itself, more resilient than the hard unreacted silica particles. Accordingly, the CSH skin may provide some protection to the unreacted silica core in addition to "enlarging" the particle such that it falls outside the respirable range.

In addition, the applicant believes the spherical shape of the CSH particle may result in the CSH particle not "keying" into and the surrounding cement as well as to the rough jagged silica crystal. Accordingly, in addition to the unreacted silica particles themselves being cut or cleaved from the surrounding cement, the CSH particles with unreacted silica core may also be removed from the surrounding cement rather than ground away by the saw blade.



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It is also possible using prereacted CSH particles rather than forming CSH in situ as in conventional techniques that the size of the CSH particles can be better controlled to avoid formation in the respirable range.

Lastly, the applicant also believes that the use of low density modifiers provide  
5 localised low density areas. When these are impacted by the cutting tooth blades, the board or article tends to fracture at the weakest point ie the localised area of low density thereby creating larger chips reducing the amount of respirable silica formed. Such localised areas of low density also assist in crack propagation improving the cutting action of the toothed blade saw.

10 In a fifth aspect, the present invention provides a method for producing a cementitious article having a reduced respirable size silica particle content, said method comprising preparing an aqueous slurry with a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide the resultant article with a density lower than  $1.2 \text{ g/cm}^3$ , forming a green shaped article  
15 and curing the green shaped article.

In a sixth aspect, the present invention provides a method for producing a cementitious article having a low propensity to release airborne respirable silica, said method comprising preparing an aqueous slurry with a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide  
20 the resultant article with a density lower than  $1.2 \text{ g/cm}^3$ , forming a green shaped article and curing the green shaped article.

In a seventh aspect, the present invention provides a method of producing a cementitious article having a reduced respirable size silica particle content comprising preparing an aqueous slurry of a cementitious material, a siliceous material and a low  
25 bulk density material which is substantially calcium silicate hydrate, forming a green shaped article and curing the green shaped article.

In an eighth aspect, the present invention provides a method of producing a cementitious article having a low propensity to release airborne respirable silica comprising preparing an aqueous slurry of a cementitious material, a siliceous material  
30 and a low bulk density material which is substantially calcium silicate hydrate, forming a green shaped article and curing the green shaped article.

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The green shaped article may be formed by any one of the following methods: use of a filter press (dewatering); the Hatschek method; the Magnani method; the Fourdrenier method; use of a forming press; strip forming or the like. It will be appreciated that in the event that the green shaped article is formed by way of an  
5 extrusion process then the aqueous slurry used will have a lower water content than those used in other forming operations. Indeed, it may have a paste like consistency.

The applicant has found that it is possible to provide a low bulk density material which is substantially composed of calcium silicate hydrate for use in a building product without it being necessary to ensure full conversion of the reactants to calcium  
10 silicate hydrate. In a preferred embodiment, this reaction is terminated prior to complete conversion of the reactants to calcium silicate hydrate. Preferably the reaction is terminated at less than 4 hours. More preferably, the reaction is conducted over a period of up to 2 hours such that at least 80% of the calcareous reactant material is converted into calcium silicate hydrate (preferably as determined from DTA  
15 (differential thermal analysis)/TGA (thermogravimetric analysis)).

The product resulting from this reaction can be used to produce cementitious products resulting in densities of  $1.2 \text{ g/cm}^3$  to  $0.5 \text{ g/cm}^3$  and if combined with aeration of the slurry, the density may be even lower.

The siliceous reactant material may be obtained in the correct particle  
20 size or alternatively ground by any appropriate method including a high impact type ball or rod mills, vertical stirred ball mill or attrition mill. Such mills obtain high particle size reduction rates by impact fracture of particles. The siliceous reactant material preferably has particle size of 90 wt % less than about 100 micron more preferably less than 70 micron and most preferably less than 50 micron diameter (as  
25 measured on a laser diffraction particle size analyser such as a Malvern Mastersizer diffraction type particle size analyser).

Suitable siliceous reactant materials are crystalline, most preferably such as quartz, quartzite sand, quartzite rock or crystalline silica. Amorphous siliceous reactant materials can also be used but are less desirable. Typical amorphous siliceous  
30 materials include diatomaceous earth, silica fume, rice hull ash, fly ash, blast furnace slag, granulated slag, steel slag, crystalline or air cooled slag, geothermal silica and

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mixtures thereof. The siliceous material added to the formulation and that used in the reaction to form the low bulk density material may be the same or different.

The silica particle size may be adjusted if desired to alter reaction rates for forming the substantially calcium silicate hydrate product. Other process parameters or additives may be altered to adjust the various properties of the resultant building product including density, toughness etc.

Suitable calcareous materials include lime particularly quick lime. Quick lime can be hydrated by slaking it in water, preferably at a temperature of 40° greater than in a ratio of 1 to 7 litres of water per kilogram of lime.

Water in the reaction is typically present in an amount to up to 30 times the total weight of the siliceous and calcareous reactant materials.

Suitably the siliceous material and calcareous material are reacted at a temperature between 120°C and 250°C, more preferably at a temperature of between 160°C and 180°C.

Preferably the siliceous and calcareous materials are reacted in a stirred pressure vessel. Suitable pressures used are typically between 200 and 4000 kPa, more preferably between 600 and 1000 kPa.

Typically, the calcareous material and siliceous material are reacted in a molar ratio of  $\text{CaO}:\text{SiO}_2$  of from 0.1 up to 1.2. More preferably they are reacted in a ratio of 0.3-0.8.

Throughout this specification, unless indicated otherwise where there is reference to wt %, all values are with respect to the formulation on a dry ingredients weight basis prior to addition of water and processing.

The siliceous material is preferably present in the dry formulation in an amount of from 10 to 80 wt %, more preferably 30 to 70 wt %, most preferably 40 to 65 wt %. Preferably the siliceous material is ground sand (silica) or fine quartz and has an average particle size of 1 to 500 microns, more preferably 20 to 70 microns.

The cementitious material is preferably present in the dry formulation in an amount of from 10 to 80 wt %, more preferably 20 to 70 wt %, most preferably 30 to 40 wt %. Suitable cementitious material is cement and/or lime and/or lime containing material and includes Portland cement, hydrated lime, lime or mixtures thereof.

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Preferably the cementitious material has a fineness index of 200 to 450m<sup>2</sup>/kg and more preferably 300 to 400m<sup>2</sup>/kg.

It will be appreciated that the siliceous material and cementitious material may originate from separate source materials eg silica and Portland cement or can  
5 originate from a single source material eg a blended cement which is a cement including ordinary Portland cement and/or off-white cement with one or a combination of limestone, granulated slag and condensed silica fume. The proportion of these additions is in excess of 5% by mass.

Similarly, the siliceous reactant material and calcareous reactant material can  
10 be provided from separate sources eg silica and limestone or from a single source material eg a siliceous limestone deposit.

The low bulk density calcium silicate hydrate of the invention is preferably added in an amount of up to 80 wt %, more preferably up to 50% of the dry formulation.

15 The cementitious product can include a fibrous material capable of producing a fibre reinforced product. Suitable fibrous materials can include asbestos however it is more preferable to use non-asbestos fibres including cellulose such as softwood and hardwood cellulose fibres, non wood cellulose fibres, mineral wool, steel fibres, synthetic polymer fibres such as polyamides, polyesters, polypropylene,  
20 polymethylpentene, polyacrylonitrile, polyacrylamide, viscose, nylon, PVC, PVA, rayon, and glass, ceramic or carbon. When cellulose fibres are used, they are preferably refined to a degree of freeness of between 20 and 800 Canadian Standard Freeness (CSF), more preferably 200 to 500 CSF. Thermomechanically or chemically refined fibres are preferred. Cellulose fibres produced by the Kraft process are  
25 suitable. The cellulose fibres may be bleached, unbleached, partially bleached or mixtures thereof. The fibrous materials may be present in a concentration of 0 to 25 wt %, preferably 2 to 16 wt %, more preferably 5 to 14 wt % based on the weight of the dry formulation.

The cementitious product may also contain 0 to 40 wt % of other additives such  
30 as fillers, for example, mineral oxides, hydroxides and clays, metal oxides and hydroxides, fire retardants, for example, magnesite or dolomite, thickeners, silica

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fume or amorphous silica, colorants, pigments, water sealing agents, water reducing agents, setting rate modifiers, hardeners, filtering aids, plasticisers, dispersants, foaming agents or flocculating agents, water-proofing agents, density modifiers or other processing aids. Specific additives can include aluminium powder, kaolin, mica, metakaolin, silica fume and calcium carbonate.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

In order that the nature of the present invention may be more clearly understood, it will now be described with reference to the following examples.

#### EXAMPLE 1

Tests were carried out to determine dust generation arising from cutting a sheet of fibre reinforced cement of the low respirable silica formulation. Monitoring equipment for respirable dust was worn by the saw operator. In between tests, the work area was cleaned by vacuum and airborne dust cleared by opening all doors and using a large fan. In all but one test, dust extraction was attached to the saw and multiple cuts were carried out on single sheets. A final test using three stacked sheets was also carried out.

Analysis of the respirable dust filters by both infrared spectroscopy and X-ray diffractometry indicated only low quartz concentrations in the respirable dust. In fact, only one sample had a measurable amount of quartz present (0.02 milligrams by XRD). This equates to about 1% respirable quartz in the dust, a relatively low level. Other filters had insufficient dust for detection of the small amount of quartz present.

The results of these tests confirmed that the low respirable silica cement formulation and articles thus produced result in a very low respirable silica content of the dust cloud. Indeed, most of the samples did not have a sufficient quantity of respirable silica. The only sample with detectable respirable silica produced a content of 1.2% of the respirable dust cloud. In other words, for a normal cutting action, a dust cloud of  $5 \text{ mg/m}^3$  would still only generate  $0.05 \text{ mg/m}^3$  of respirable silica which is well within the current accepted permissible exposure levels.

## EXAMPLE 2

Two samples each of the inventive low density formulation (density = 0.83 g/cm<sup>3</sup>) were compared with a conventional product (density = 1.3 g/cm<sup>3</sup>) as a control. Details of each are given in Table 1.

TABLE 1

COMPONENT	LOW DENSITY	CONTROL
Cellulose pulp	11%	8%
Cement/Sand	70%	88%
Calcium silicate	17%	nil
Other	2%	4%

Equal volumes of the low density product and control were removed by cutting, and dust samples were collected by vacuum extraction through a wet filter paper affixed to the rear of the saw assembly. The saw used was a circular saw with an 80 tooth 300 mm tungsten carbide tipped saw blade.

The dust samples were weighed. They were then digested in 1M HCl to remove hydrated silicates, and then further digested in 1 M NaOH to remove organic material, including pulp. The samples were then ignited at 1000°C to leave only a quartz residue. The quartz residue mass was measured. The sample was then dispersed in water and the particle size distribution was measured using laser light scattering (Malvern Mastersizer-X). The volume percentage less than 4.8 microns was measured.

Results are shown in Table 2.

TABLE 2

MEASURED PROPERTY	LOW DENSITY SAMPLE	CONTROL
Mass of dust collected	1.83 mg, 1.53 mg	2.53 mg, 2.50 mg
% of Quartz in dust sample	22.2%, 19.8%	39.8%, 39.7%

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Mass of quartz in dust sample	408 mg, 402 mg	1009 mg, 995 mg
% of Respirable quartz of total dust sample (mean values)	1.35%	3.43%
% of Respirable quartz of total quartz (mean values) (<5 microns Volume average)	6.38%	8.61%
Mass of respirable quartz (mean values) (<5 microns volume average)	22.6%	86.3%

It can be seen from these results that from the same volume of cut in the control material significantly less dust was collected than from the low density product (a 33% reduction in dust).

5 Further, the dust from the low density product contained less quartz (21% for low density versus 39.8% for control - a 47% decrease in total quartz).

The quartz from the low density product contained less respirable quartz (6.38% for low density versus 8.61% for control), and accordingly the dust from the low density product contained less respirable quartz (1.35% for low density versus 3.43%  
10 for control).

### EXAMPLE 3

An automatic device was built and put into service to evaluate the dust levels generated in the cutting of fibre cement planks of low respirable silica formulation. This device was also designed to replicate the same cutting motions used by installers  
15 in the cutting of fibre cement products. As a control, regular density (density = 1.3 g/cm<sup>3</sup>) fibre cement material was also tested. Two types of circular saws were used, one with a direct drive between the motor and the blade the other with a worm drive. Both saws were fitted with a conventional toothed poly-crystalline diamond blade. A room was built to totally enclose the cutting portion of the saw rig approximately 20  
20 cubic metres. Twenty five cuts were made on 8mm x 210mm fibre cement product

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stacked 4 high. Therefore, 100 boards in total were cut. The cutting interval was 30 seconds (from the time the boards were cut until the start of the next cut). Dust samples were collected using a 10mm nylon cyclone at a flowrate of 1.7 l/min. These samples were collected for the entire time of the cutting period. Upon completion of  
5 the last cycle a period of 2.5 minutes was allowed to elapse before the pumps were shut-off, the samples removed, and the chamber evacuated. These samples were then sent to an accredited laboratory and analysed using X-ray diffractometry.

The results of these tests confirm that the low respirable cement formulation article produced considerably less respirable silica than that of the regular density  
10 product. The average of respirable silica collected on the filter at the completion of testing drops from 6.45% for regular density material to 0.5% for low respirable cement formulation using the worm drive saw. Similar results were found using the direct drive saw where there was a drop from 6.97% for regular density to 0.57% for low respirable cement formulation. In both cases this represents a reduction of more  
15 than 12 times.

It will be understood that the present invention may be embodied in other forms without departing from the spirit or scope of the inventive idea as described herein.



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## CLAIMS

1. A formulation for producing a shaped cementitious article having a reduced respirable size silica particle content, said formulation comprising a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide a density of the resultant cementitious article of lower than  $1.2 \text{ g/cm}^3$ .
2. A formulation according to Claim 1 wherein the article has a density between  $1.2$  and  $0.5 \text{ g/cm}^3$ .
3. A formulation according to Claim 1 or Claim 2 wherein the low bulk density modifier is substantially pre-reacted calcium silicate hydrate.
4. A formulation according to any one of Claims 1 to 3 wherein the low bulk density modifier has a bulk density between  $0.06$  and  $0.6 \text{ g/cm}^3$ .
5. A formulation according to any one of Claims 1 to 4 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a ratio between  $0.1$  and  $1.2$ .
6. A formulation according to Claim 6 wherein the ratio of calcareous material to siliceous material is between  $0.3$  and  $0.8$ .
7. A formulation according to Claim 5 or Claim 6 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
8. A formulation according to any one of Claims 5 to 7 wherein the reaction is conducted over a period of up to four hours such as at least  $80\%$  of the calcareous reactant material is converted to calcium silicate hydrate.
9. A formulation according to any one of Claims 5 to 8 wherein the reaction is conducted over a period of up to two hours such as at least  $80\%$  of the calcareous reactant material is converted to calcium silicate hydrate.
10. A formulation according to any one of the preceding claims wherein the low density modifier includes one or more modifiers from the group consisting of fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.

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11. A formulation according to any one of the preceding claims wherein between 10 and 80% of siliceous material is included in the cementitious article.
12. A formulation according to any one of the preceding claims wherein between 40 and 65% of siliceous material is included in the cementitious article.
- 5 13. A formulation according to any one of the preceding claims wherein between 10 and 80% of cementitious material is included in the cementitious article.
14. A formulation according to any one of the preceding claims wherein between 30 and 40% of cementitious material is included in the cementitious article.
15. A formulation according to any one of the preceding claims wherein up to 80%  
10 of low bulk density modifier is included in the cementitious article.
16. A formulation according to any one of the preceding claims wherein up to 50% of low bulk density modifier is included in the cementitious article.
17. A formulation according to any one of the preceding claims wherein  
15 cementitious article includes fibrous material capable of producing a fibre reinforced product.
18. A formulation for producing a shaped cementitious article having a low propensity to release airborne respirable silica, said formulation comprising a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide a density of the resultant cementitious article of  
20 lower than  $1.2 \text{ g/cm}^3$ .
19. A formulation according to Claim 18 wherein the article has a density between 1.2 and  $0.5 \text{ g/cm}^3$ .
20. A formulation according to Claim 18 or Claim 19 wherein the low bulk density modifier is substantially pre-reacted calcium silicate hydrate.
- 25 21. A formulation according to any one of Claims 18 to 20 wherein the low bulk density modifier has a bulk density between  $0.06$  and  $0.6 \text{ g/cm}^3$ .
22. A formulation according to any one of Claims 18 to 21 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a ratio between 0.1 and 1.2.
- 30 23. A formulation according to Claim 22 wherein the ratio of calcareous material to siliceous material is between 0.3 and 0.8.

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24. A formulation according to Claim 22 or Claim 23 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
25. A formulation according to any one of Claims 22 to 24 wherein the reaction is  
5 conducted over a period of up to four hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
26. A formulation according to any one of Claims 22 to 25 wherein the reaction is conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
- 10 27. A formulation according to any one of Claims 18 to 26 wherein the low density modifier includes one or more modifiers selected from the group consisting of fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.
28. A formulation according to any one of Claims 18 to 27 wherein between 10 and  
15 80% of siliceous material is included in the cementitious article.
29. A formulation according to any one of Claims 18 to 28 wherein between 40 and 65% of siliceous material is included in the cementitious article.
30. A formulation according to any one of Claims 18 to 29 wherein between 10 and 80% of cementitious material is included in the cementitious article.
- 20 31. A formulation according to any one of Claims 18 to 30 wherein between 30 and 40% of cementitious material is included in the cementitious article.
32. A formulation according to any one of Claims 18 to 31 wherein up to 80% of low bulk density modifier is included in the cementitious article.
33. A formulation according to any one of Claims 18 to 32 wherein up to 50% of  
25 low bulk density modifier is included in the cementitious article.
34. A formulation according to any one of Claims 18 to 33 wherein cementitious article includes fibrous material capable of producing a fibre reinforced product.
35. A formulation for producing a shaped cementitious article having a reduced respirable size silica particle content, said formulation comprising a  
30 cementitious material, a siliceous material and a low bulk density material being substantially calcium silicate hydrate.

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36. A formulation according to Claim 35 wherein the article has a density between 1.2 and 0.5 g/cm<sup>3</sup>.
37. A formulation according to any one of Claim 35 or Claim 36 wherein the low bulk density modifier has a bulk density between 0.06 and 0.6 g/cm<sup>3</sup>.
- 5 38. A formulation according to any one of Claims 35 to 37 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a ratio between 0.1 and 1.2.
39. A formulation according to Claim 38 wherein the ratio of calcareous material to siliceous material is between 0.3 and 0.8.
- 10 40. A formulation according to Claim 38 or Claim 39 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
41. A formulation according to any one of Claims 38 to 40 wherein the reaction is conducted over a period of up to four hours such as at least 80% of the
- 15 calcareous reactant material is converted to calcium silicate hydrate.
42. A formulation according to any one of Claims 38 to 41 wherein the reaction is conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
43. A formulation according to any one of Claims 35 to 42 wherein the low density
- 20 modifier includes one or more modifiers selected from the group consisting of fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.
44. A formulation according to any one of Claims 35 to 43 wherein between 10 and 80% of siliceous material is included in the cementitious article.
- 25 45. A formulation according to any one of Claims 35 to 44 wherein between 40 and 65% of siliceous material is included in the cementitious article.
46. A formulation according to any one of Claims 35 to 45 wherein between 10 and 80% of cementitious material is included in the cementitious article.
47. A formulation according to any one of Claims 35 to 46 wherein between 30 and
- 30 40% of cementitious material is included in the cementitious article.

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48. A formulation according to any one of Claims 35 to 47 wherein up to 80% of low bulk density modifier is included in the cementitious article.
49. A formulation according to any one of Claims 35 to 48 wherein up to 50% of low bulk density modifier is included in the cementitious article.
- 5 50. A formulation according to any one of Claims 35 to 49 wherein cementitious article includes fibrous material capable of producing a fibre reinforced product.
51. A formulation for producing a shaped cementitious article having a low propensity to release airborne respirable silica, said formulation comprising a cementitious material, a siliceous material and a low bulk density material being
- 10 substantially calcium silicate hydrate.
52. A formulation according to Claim 51 wherein the article has a density between 1.2 and 0.5 g/cm<sup>3</sup>.
53. A formulation according to any one of Claim 51 or Claim 52 wherein the low bulk density modifier has a bulk density between 0.06 and 0.6 g/cm<sup>3</sup>.
- 15 54. A formulation according to any one of Claims 51 to 53 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a ratio between 0.1 and 1.2.
55. A formulation according to Claim 54 wherein the ratio of calcareous material to siliceous material is between 0.3 and 0.8.
- 20 56. A formulation according to Claim 54 or Claim 55 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
57. A formulation according to any one of Claims 54 to 56 wherein the reaction is conducted over a period of up to four hours such as at least 80% of the
- 25 calcareous reactant material is converted to calcium silicate hydrate.
58. A formulation according to any one of Claims 54 to 57 wherein the reaction is conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
59. A formulation according to any one of Claims 54 to 58 wherein the low density
- 30 modifier includes one or more modifiers selected from the group consisting of

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fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.

60. A formulation according to any one of Claims 51 to 59 wherein between 10 and 80% of siliceous material is included in the cementitious article.
- 5 61. A formulation according to any one of Claims 51 to 60 wherein between 40 and 65% of siliceous material is included in the cementitious article.
62. A formulation according to any one of Claims 51 to 61 wherein between 10 and 80% of cementitious material is included in the cementitious article.
63. A formulation according to any one of Claims 51 to 62 wherein between 30 and 10 40% of cementitious material is included in the cementitious article.
64. A formulation according to any one of Claims 51 to 63 wherein up to 80% of low bulk density modifier is included in the cementitious article.
65. A formulation according to any one of Claims 51 to 64 wherein up to 50% of low bulk density modifier is included in the cementitious article.
- 15 66. A formulation according to any one of Claims 51 to 65 wherein cementitious article includes fibrous material capable of producing a fibre reinforced product.
67. A method for producing a cementitious article having a reduced respirable size silica particle content, said method comprising preparing an aqueous slurry with a cementitious material, a siliceous material and a low bulk density modifier in a 20 quantity sufficient to provide the resultant article with a density lower than 1.2 g/cm<sup>3</sup>, forming a green shaped article and curing the green shaped article.
68. A method according to Claim 67 wherein the article has a density between 1.2 and 0.5 g/cm<sup>3</sup>.
69. A method according to Claim 67 or Claim 68 wherein the low bulk density 25 modifier is substantially pre-reacted calcium silicate hydrate.
70. A method according to any one of Claims 67 to 69 wherein the low bulk density modifier has a bulk density between 0.06 and 0.6 g/cm<sup>3</sup>.
71. A method according to any one of Claims 67 to 70 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a 30 ratio between 0.1 and 1.2.

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72. A method according to any Claim 71 wherein the ratio of calcareous material to siliceous material is between 0.3 and 0.8.
73. A method according to Claim 71 or Claim 72 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete  
5 conversion of the reactants to calcium silicate hydrate.
74. A method according to any one of Claims 71 to 73 wherein the reaction is conducted over a period of up to four hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
75. A method according to any one of Claims 71 to 74 wherein the reaction is  
10 conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
76. A method according to any one of Claims 67 to 75 wherein the low density modifier includes one or more modifiers selected from the group consisting of fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene  
15 and chemical or mechanical gas entrainment.
77. A method according to any one of Claims 67 to 76 wherein between 10 and 80% of siliceous material is included in the cementitious article.
78. A method according to any one of Claims 67 to 77 wherein between 40 and 65% of siliceous material is included in the cementitious article.
- 20 79. A method according to any one of Claims 67 to 78 wherein between 10 and 80% of cementitious material is included in the cementitious article.
80. A method according to any one of Claims 67 to 79 wherein between 30 and 40% of cementitious material is included in the cementitious article.
81. A method according to any one of Claims 67 to 80 wherein up to 80% of low  
25 bulk density modifier is included in the cementitious article.
82. A method according to any one of Claims 67 to 81 wherein up to 50% of low bulk density modifier is included in the cementitious article.
83. A method according to any one of Claims 67 to 82 wherein said cementitious article includes fibrous material capable of producing a fibre reinforced product.

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84. A method according to any one of Claims 67 to 83 wherein said green shaped article is formed by extrusion, Hatschek, Magnani, Fourdrenier, filter pressing, form pressing, slip forming or the like.
85. A method for producing a cementitious article having a low propensity to  
5 release airborne respirable silica, said method comprising preparing an aqueous slurry with a cementitious material, a siliceous material and a low bulk density modifier in a quantity sufficient to provide the resultant article with a density lower than  $1.2 \text{ g/cm}^3$ , forming a green shaped article and curing the green shaped article.
- 10 86. A method according to Claim 85 wherein the article has a density between 1.2 and  $0.5 \text{ g/cm}^3$ .
87. A method according to Claim 85 or Claim 86 wherein the low bulk density modifier is substantially pre-reacted calcium silicate hydrate.
88. A method according to any one of Claims 85 to 87 wherein the low bulk density  
15 modifier has a bulk density between  $0.06$  and  $0.6 \text{ g/cm}^3$ .
89. A method according to any one of Claims 85 to 88 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a ratio between 0.1 and 1.2.
90. A method according to Claim 89 wherein the ratio of calcareous material to  
20 siliceous material is between 0.3 and 0.8.
91. A method according to Claim 89 or Claim 90 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
92. A method according to any one of Claims 89 to 91 wherein the reaction is  
25 conducted over a period of up to four hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
93. A method according to any one of Claims 89 to 92 wherein the reaction is conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
- 30 94. A method according to any one of Claims 85 to 93 wherein the low density modifier includes one or more modifiers selected from the group consisting of



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fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.

95. A method according to any one of Claims 85 to 94 wherein between 10 and 80% of siliceous material is included in the cementitious article.
- 5 96. A method according to any one of Claims 85 to 95 wherein between 40 and 65% of siliceous material is included in the cementitious article.
97. A method according to any one of Claims 85 to 96 wherein between 10 and 80% of cementitious material is included in the cementitious article.
98. A method according to any one of Claims 85 to 97 wherein between 30 and 40%  
10 of cementitious material is included in the cementitious article.
99. A method according to any one of Claims 85 to 98 wherein up to 80% of low bulk density modifier is included in the cementitious article.
100. A method according to any one of Claims 85 to 99 wherein up to 50% of low bulk density modifier is included in the cementitious article.
- 15 101. A method according to any one of Claims 85 to 100 wherein said cementitious article includes fibrous material capable of producing a fibre reinforced product.
102. A method according to any one of Claims 85 to 101 wherein said green shaped article is formed by extrusion, Hatschek, Magnani, Fourdrenier, filter pressing, form pressing, slip forming or the like.
- 20 103. A method of producing a cementitious article having a reduced respirable size silica particle content comprising preparing an aqueous slurry of a cementitious material, a siliceous material and a low bulk density material which is substantially calcium silicate hydrate, forming a green shaped article and curing the green shaped article.
- 25 104. A method according to Claim 103 wherein the article has a density between 1.2 and  $0.5 \text{ g/cm}^3$ .
105. A method according to any Claim 103 or Claim 104 wherein the low bulk density modifier has a bulk density between  $0.06$  and  $0.6 \text{ g/cm}^3$ .
106. A method according to any one of Claims 103 to 105 wherein the low bulk  
30 density modifier is produced by reacting siliceous material with calcareous material in a ratio between 0.1 and 1.2.

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107. A method according to any Claim 106 wherein the ratio of calcareous material to siliceous material is between 0.3 and 0.8.
108. A method according to Claim 106 or Claim 107 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
- 5 109. A method according to any one of Claims 106 to 108 wherein the reaction is conducted over a period of up to four hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
110. A method according to any one of Claims 106 to 109 wherein the reaction is conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
- 10 111. A method according to any one of Claims 103 to 110 wherein the low density modifier includes one or more modifiers selected from the group consisting of fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.
- 15 112. A method according to any one of Claims 103 to 111 wherein between 10 and 80% of siliceous material is included in the cementitious article.
113. A method according to any one of Claims 103 to 112 wherein between 40 and 65% of siliceous material is included in the cementitious article.
- 20 114. A method according to any one of Claims 103 to 113 wherein between 10 and 80% of cementitious material is included in the cementitious article.
115. A method according to any one of Claims 103 to 114 wherein between 30 and 40% of cementitious material is included in the cementitious article.
116. A method according to any one of Claims 103 to 115 wherein up to 80% of low bulk density modifier is included in the cementitious article.
- 25 117. A method according to any one of Claims 103 to 116 wherein up to 50% of low bulk density modifier is included in the cementitious article.
118. A method according to any one of Claims 103 to 117 wherein said cementitious article includes fibrous material capable of producing a fibre reinforced product.

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119. A method according to any one of Claims 103 to 118 wherein said green shaped article is formed by extrusion, Hatschek, Magnani, Fourdrenier, filter pressing, form pressing, slip forming or the like.
120. A method of producing a cementitious article having a low propensity to release airborne respirable silica comprising preparing an aqueous slurry of a cementitious material, a siliceous material and a low bulk density material which is substantially calcium silicate hydrate, forming a green shaped article and curing the green shaped article.
121. A method according to Claim 120 wherein the article has a density between 1.2 and 0.5 g/cm<sup>3</sup>.
122. A method according to any Claim 120 or Claim 121 wherein the low bulk density modifier has a bulk density between 0.06 and 0.6 g/cm<sup>3</sup>.
123. A method according to any one of Claims 120 to 122 wherein the low bulk density modifier is produced by reacting siliceous material with calcareous material in a ratio between 0.1 and 1.2.
124. A method according to any Claim 123 wherein the ratio of calcareous material to siliceous material is between 0.3 and 0.8.
125. A method according to Claim 123 or Claim 124 wherein the reaction between the calcareous material and siliceous material is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
126. A method according to any one of Claims 123 to 125 wherein the reaction is conducted over a period of up to four hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
127. A method according to any one of Claims 123 to 126 wherein the reaction is conducted over a period of up to two hours such as at least 80% of the calcareous reactant material is converted to calcium silicate hydrate.
128. A method according to any one of Claims 120 to 127 wherein the low density modifier includes one or more modifiers selected from the group consisting of fly ash, hollow fly ash, hollow ceramic spheres, perlite, vermiculite, polystyrene and chemical or mechanical gas entrainment.

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129. A method according to any one of Claims 120 to 128 wherein between 10 and 80% of siliceous material is included in the cementitious article.
130. A method according to any one of Claims 120 to 129 wherein between 40 and 65% of siliceous material is included in the cementitious article.
- 5 131. A method according to any one of Claims 120 to 130 wherein between 10 and 80% of cementitious material is included in the cementitious article.
132. A method according to any one of Claims 120 to 131 wherein between 30 and 40% of cementitious material is included in the cementitious article.
- 10 133. A method according to any one of Claims 120 to 132 wherein up to 80% of low bulk density modifier is included in the cementitious article.
134. A method according to any one of Claims 120 to 133 wherein up to 50% of low bulk density modifier is included in the cementitious article.
135. A method according to any one of Claims 120 to 134 wherein said cementitious article includes fibrous material capable of producing a fibre reinforced product.
- 15 136. A method according to any one of Claims 120 to 135 wherein said green shaped article is formed by extrusion, Hatschek, Magnani, Fourdrenier, filter pressing, form pressing, slip forming or the like.
137. A formulation for producing a shaped cementitious article having a reduced respirable size silica particle content substantially as herein described.
- 20 138. A formulation for producing a shaped cementitious article having a low propensity to release airborne respirable silica substantially as herein described.
139. A method for producing a shaped cementitious article having a reduced respirable size silica particle content substantially as herein described.
140. A method for producing a shaped cementitious article having a low propensity to release airborne respirable silica substantially as herein described.
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00875

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>6</sup> : C04B 28/18, 28/20, 38/00, 38/08, 40/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) C04B 28/-, 38/-, 40/-, 14/-, 18/-		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched -		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT, JAPIO, USPTO (Full text)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/45222 A (James Hardie) 15 October 1998 & ZA 9803063 13 October 1998 See whole document	1-140
X	WO 98/38139 A (Schwenk) 3 September 1998 See page 2 line 18 to page 3 line 16 & page 4	1, 18, 35, 51, 67, 85, 103, 120
X	EP 282016 A (Redco) 14 September 1998 See Example 1 & page 1	1, 18, 35, 51, 67, 85, 103, 120
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" Document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 10 December 1999		Date of mailing of the international search report 22 DEC 1999
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No.: (02) 6285 3929		Authorized officer  JAMES DZIEDZIC Telephone No.: (02) 6283 2495

# INTERNATIONAL SEARCH REPORT

international application No.

PCT/AU 99/00875

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 2617218 A (Showa) 27 October 1977 See Examples	1, 18, 35, 51, 67, 85, 103, 120
X	Derwent Abstract Accession No 78-48983a, Class L02, JP 78017610 (Kontek) 9 June 1978	1, 18, 35, 51, 67, 85, 103, 120
X	Japatic Abstract of JP 08 217561 A ( Chichibu Onoda Cement) 27 August 1996 CD Vol MIJP 9608 PAJ	1, 18, 35, 51, 67, 85, 103, 120
X	Japatic Abstract of JP 08217564 A (Sumitomo) 27 August 1996 CD Vol MIJP 9608 PAJ	1, 18, 35, 51, 67, 85, 103, 120
X	Japatic Abstract of JP 07101787 A (Sumitomo) 18 April 1995 CD Vol MIJP 9504 PAJ	1, 18, 35, 51, 67, 85, 103, 120
X	Japatic Abstract of JP 03141172 A (Sumitomo) 17 June 1991 CD Vol MIJP 002C PAJ	1, 18, 35, 51, 67, 85, 103, 120
X	US 4162924 A (Kubo) 31 July 1979 See Abstract, Claim 1	1,18,35,51,67,85, 103,120
X	US 4613472 A (Suanholm) 23 September 1986 See col 1 lines. 6-23, col 5 lines 1-9	1,8,35,51,67, 85,103,120
X	US 5330573 A (Nakano) 19 July 1994 See abstract, claims	1,18,35,51,67, 85,103,120
X	US 5580378 A (Shulman) 3 December 1996 See abstract, Exs : & claim 30	1,18,35,51,67, 85,103,120
X	US 4210457 A (Dodson) 1 July 1980 See abstract. claims 25-26	1,18,35,51,67, 85,103,120

# INTERNATIONAL SEARCH REPORT

## Information on patent family members

International application No.  
PCT/AU 99/00875

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	9845222	AU	69111/98	ZA	9803063		
WO	9838139	AU	67250/98	CA	2230329	DE	19707700
EP	282016	JP	63314250	US	5120775		
US	4162924	BR	7700875	CA	1106142	DE	2705828
		GB	1539141	JP	52098021		
US	4613472	CA	1240123	DE	3402145	SE	8300342
		US	4902211				
US	5330573	CA	2093652	EP	562112	JP	3237051
		WO	9302986				
US	5580378	US	5622556	US	5725652		
US	4210457	CA	1129444				
END OF ANNEX							